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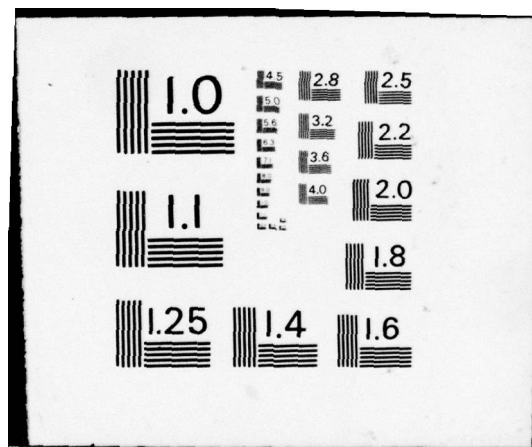
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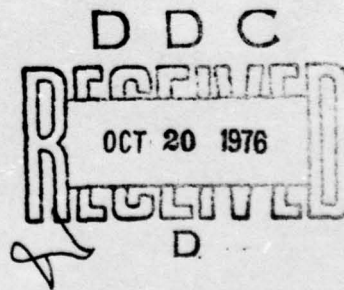
FINAL REPORT

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PROPERTIES OF POLYMERS

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Frank E. Karasz



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FINAL REPORT

EFFECT OF STRUCTURE ON PHYSICAL
PROPERTIES OF POLYMERS

GRANT AFOSR 72-2170

1 November 1971-28 February 1976

Frank E. Karasz
Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01002

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CONTENTS

- I. Title
- II. Principal Investigator
- III. Grant Number
- IV. Dates
- V. Senior Research Personnel
- VI. Junior Research Personnel
- VII. Abstract of Accomplishments
- VIII. Description of Research Undertaken
 - A. Poly (α -chloroacrylates)
 - B. Interaction of Water with Segmented Polyurethanes
 - C. Quasi-Elastic Light Scattering
 - D. Vibrations in Thick Beams
 - E. Polymer-Polymer Interactions
 - F. High Pressure Studies
 - G. Other Studies
- IX. Publications

- I. TITLE: Effect of Structure on Physical Properties of
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Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01002
- III. GRANT NUMBER: AFOSR 72-2170
- IV. DATES: 1 November 1971 - 28 February 1976.
- V. SENIOR RESEARCH PERSONNEL: Dr. H. Goettler
Dr. R. Hammel
Dr. O. Heybey
Dr. W. Wenig
- VI. JUNIOR RESEARCH PERSONNEL: P. Alexandrovich
G.R. Dever
J.R. Fried
L. Kleiner
R. Neira
K. Rozkuszka
E.B. Wilusz
S. Wunder

VII. ABSTRACT OF ACCOMPLISHMENTS.

The overall objective of the program has been to examine the effect of variations in the chemical and stereochemical structure of a polymer on its physical, mechanical and electrical properties. Such information is of interest both on a fundamental level and because of its implications in the design of macromolecular structures for specific applications. Within this general direction a number of different investigations were undertaken. These are described below.

The effect of configuration--stereochemical structure--in poly- α -chloroacrylic acid esters was studied. These unsymmetrically disubstituted vinyl polymers showed a large dependence of T_g on tacticity in accordance with theory developed earlier. Other transitional and thermodynamic properties were also found to be structure-dependent. The effect of chemical structure was demonstrated in a different context in an investigation of the interaction of small molecules, especially water, with a series of segmented polyurethanes with systematically varying soft segment compositions. Decreasing hydrophilicity of the latter substantially affected transport properties. Evidence for the amorphous nature of the bound water layer was obtained from comparison of the glass transition behavior of the dry and water-containing polymers.

The effect of structure is particularly profound in the area of polymer-polymer compatibility. Extremely small changes in composition in either or both constituents of a given binary system may be sufficient to remove the system from a compatible to an incompatible regime. These and other effects were studied in considerable detail in an on-going investigation of interactions between poly(2,6-dimethyl phenylene oxide) and polystyrene, together with stereochemical and chemical modifications of the latter polymer. Thermodynamic, mechanical and electrical properties of these systems were studied with the goal of determining characteristics general to all compatible systems and of finding methods of predicting behavior.

The solid and liquid state properties of a given ensemble of polymers are functions of temperature, pressure, and in the case of visco-elastic related phenomena; stress frequency. We have studied the effect of these three parameters in a dynamical mechanical investigation of polymethyl methacrylate. Although important, the effect of pressure on mechanical relaxation of any polymer has only rarely been examined. In the study undertaken here the effect of pressure on both the α - and β -relaxations was analyzed. In another experiment, apparatus for measuring the effect of pressure on the lattice dimensions of poly-

mer crystals was developed and tested in a broad study of the polyethylene lattice. The linear compressibilities thus obtained permitted a detailed comparison with theoretically predicted equations of state for this macromolecule. A further dynamical mechanical experiment was concerned with resonant vibrations in thick beams. From measurements and analysis of higher mode resonances the contributions of shear and elongational deformation could be separately obtained, thereby providing a complete elastic characterization of an isotropic material. We have also been concerned in one study with the properties of solvated macromolecules, in this case an ionizable copolymer of acrylic acid and ethyl acrylate. The experimental technique used was quasi-elastic light scattering in which the spectral broadening and shape of light scattered from spontaneously occurring density fluctuations within the solution is measured with a homodyne spectrometer. The translational diffusion constant is obtained from such data together with the effects of hydrodynamic and thermodynamic solute-solute and solute-solvent interactions as a function of solute concentration, pH, ionic strength and temperature. Finally a number of miscellaneous studies dealing with bulk properties of polymers were completed and are described in the text of this report.

VIII DESCRIPTION OF RESEARCH ACCOMPLISHED

The research accomplished during the grant period may be divided into the following areas:

A. Poly(α -chloroacrylates).

During a previous grant period the P.I. proposed a theoretical basis for the effect of structure of the glass transition of mono- and disubstituted vinyl polymers [F.E. Karasz and W.J. MacKnight (Macromolecules 1, 537 1968)]. The predictions of the theory were that stereoregularity should have no effect on T_g in the case of mono-substituted polymers but that T_g should be a function of stereoregularity for the unsymmetrically disubstituted vinyl polymers. Such data as were available at that time were consistent with the theory. To further investigate this problem a more comprehensive approach involving the synthesis and characterization of several esters of poly(α -chloroacrylic acid) as a function of stereoregularity was instituted. The research, involving inter alia, the exploration of new stereoregular catalyst systems (1), succeeded to the extent that atactic, syndiotactic and isotactic isomers of the methyl, ethyl and propyl esters of the polyacid were obtained. A number of methyl-ethyl copolymers were also synthesized. The complete characterization of these polymers in

terms of their molecular weights, tacticity and transitional properties was undertaken using a wide variety of experimental techniques. The all-important determination of triad, tetrad, and (in some cases) pentad tacticities was a major task involving many high resolution (220 and 300 MHz) NMR measurements together with concomitant computer analyses (2). Transitional and relaxational behavior of the esters as a function of tacticity were explored with dielectric and dynamical mechanical relaxation measurements and differential scanning calorimetry (3).

The poly(α -chloroacrylates) proved to be interesting polymers per se. It was found possible for example to explicitly assign all the tetrad peaks in the NMR studies of the methyl ester and to successfully compare experimental triad tacticities taken from pendant ester group data with these calculated from backbone tetrad data, (2). The glass transition temperatures of the stereoregular polymers were shown to be strong functions of tacticity with a T_g difference of some 94°C for the isotactic-syndiotactic methyl ester pair. The original theory had predicted a ΔT_g of some 112°C . The isotactic polyesters were found to be slightly crystalline (T_m 's and ΔH_f 's were determined calorimetrically) and relaxational studies provided some evidence for a β -relaxation associated with pendant group rotation, (3).

B. Interaction of Water with Segmented Polyurethanes.

A comprehensive study of the effect of structure in the interaction of water with segmented block polyurethanes was undertaken. The program started with the synthesis of a series of polymers of the general structure $MS[(MB)_xMS]_yM$ where $M \equiv$ methylene diphenylene diisocyanate, $B \equiv$ 1,4-butanediol and $S \equiv$ a block polymeric glycol of M.W 2000 and varying structures ranging from polyethylene oxide to polypropylene oxide with intermediate copolymers. The parameter x ranged from 0 to 5, y equaled 30 for all members of the series. These polyurethanes are elastomeric at room temperature and thermoplastic because of the presence of physically crosslinking "hard" (MB) segments in a "soft" (S) matrix, (4). Permeation of a number of small molecules through membranes prepared from these polymers were measured by a modified time lag technique with flowing carrier-gas. Permeants studied included helium, nitrogen, argon and water, and measurements were performed from 10° - 90° C. Analysis of the results for the permanent gases in terms of Fickian theory proved successful but the hydrophilicity of the structure and the consequent special interactions yielded very complex behavior in the case of water, (5). A more elaborate characterization of the polymers in terms of their interaction with water was instituted involving water uptake, transmission

and sorption studies. Considerable additional information was obtained from later calorimetric measurements which clearly demonstrated the presence of layers of "bound" water in the hydrophilic polyether soft segments. We were able to show, for the first time, that this water was able to depress the T_g of the polyether in a systematic fashion thus lending strong support to hypotheses concerning the amorphous nature of this water, (4).

Composition was also found to be extremely important in sorption and diffusional behavior in the system. Thus, although diffusion coefficients decreased with increasing sorbed water concentration as the ratio of polyethylene oxide increased, a result attributed to clustering, some interference from the hard blocks domains leading to an increase in D_T as a function of water uptake was noted in other studies.

In addition to the transport studies described above a more general characterization of these polymers was undertaken. Phase-separation, domain formation and crystallization investigations using electron-microscopy, relaxational and x-ray techniques were performed on polymers whose chemical structure had been varied in systematic fashion, (5).

C. Quasi-elastic Light Scattering.

The development of optical heterodyne techniques for spectral line-width studies of light scattered from polymer solutions in the past decade has yielded an important new tool for the characterization of the size and conformation of macromolecular chains in dilute solution. Experimental techniques of considerable sophistication involving photon-counting and subsequent quasi-real time Fourier transformations and/or autocorrelation function computation have been developed which permit the rapid and precise measurement of translational diffusion constants for such macromolecules under a variety of conditions. We have applied such techniques to several studies of synthetic polymers and developed improved analyses of spectral line shapes to yield information on polymer molecular weight dispersion, (6).

More recently we have explored in considerable detail the conformational properties of a polyelectrolyte, a random copolymer of ethyl acrylate and acrylic acid. (This copolymer is also soluble in unionized form in several organic solvents) The effect of pH and ionic strength on D_T has been explored both as a function of M.W. and solute concentration. Second virial coefficients characterizing the thermodynamic behavior of this system are known from earlier studies but the present

measurements have yielded new and valuable information on hydrodynamic solute-solute and solute-solvent interactions. In chemically similar systems the existence of a coil-coil conformational transition has been postulated for some time on the basis of several solution thermodynamic measurements; our D_T results appear to lend some support to this claim, (7).

D. Vibrations in Thick Beams.

Resonant frequency and amplitude decay measurements of polymeric samples in the form of thin beams--reeds--have long been used as a comparatively simple method of characterizing the dynamical mechanical characteristics of such materials. The quantities obtained from such studies are principally $E'(\omega)$ and $E''(\omega)$, the frequency dependent elongational storage and loss moduli respectively. The complete determination of the elastic properties of an isotropic material requires measurement of a second quantity e.g. the shear modulus G , or Poisson's ratio ν . The analysis of flexural vibrations in a thick beam though experimentally and mathematically more complex offered the possibility of a complete determination of the corresponding elastic properties in a single set of measurements, since vibrations in such beams involve shear as well as longitudinal deformation.

An experimental technique has been developed here to utilize this concept by measuring with high precision resonant frequencies of sample beams up to the tenth or higher mode. A parallel theoretical development has then enabled us to analyze such data to yield both shear and elongational moduli, (8).

The theory involves a perturbation treatment of the Bernouilli-Euler equation describing motion of a thick rectangular beam (in the clamped-free configuration) which yields ultimately the equation.

$$\frac{\omega_{BN}}{\omega_N} = 1 + (1+M)(a^2/L^2) C_N$$

where ω_{BN} and ω_N are respectively the Bernouilli-Euler and measured Nth mode resonant frequencies; $M = E/kG$ (k being the so-called Timoshenko shear coefficient); a^2/L^2 are geometrical beam parameters and C_N is a E' . C_N is a mode number which includes an explicit functional relation to $E'(\omega)$. By measuring ω_N (accuracies of the order of 0.1 - 0.2% are required) we can extract the desired quantities E' , G' and ν . E'' can be obtained from concomitant decay determinations.

In tests of the system using aluminum bars highly satisfactory results were obtained. As a by-product it was found possible to establish, for the first time, numerical values for two parameters (the shear coefficient and the clamped-end correction factor). Measurements on polymeric beams were also satisfactory and paved the way for useful studies of the elastic properties of a wide variety of composite systems, (9).

E. Polymer-polymer Interactions.

A considerable fraction of total resources during the grant period has been devoted to the study of polymer-polymer interactions in compatible multi-component macromolecular systems. The importance of this phenomenon both in terms of fundamental science and in material technology is sufficient to justify the commitment of considerable effort to this area.

The behavior of binary systems consisting of both a macromolecular solute and solvent is quite poorly understood in comparison to the theoretical and experimental descriptions currently available for polymer-low molecular weight solvent systems. This is a reflection both of the relative scarcity of compatibility in polymers and of the difficulty of establishing the equilibrium existence of molecular miscibility in such systems.

Our approach has concentrated on the detailed study of poly(2,6-dimethyl phenylene oxide) (PPO) and polystyrene (PS) together with polymers of closely related chemical structures. This hierarchy of binary combinations offers a great deal of versatility in that amorphous-amorphous, amorphous-crystalline and crystalline-crystalline systems can be obtained. By copolymerization of the PS with, for example, p-chlorostyrene we can, in addition, examine the critical very narrow transition between compatible and incompatible regimes.

For a complete description the reader is referred to the several published papers in this area, (10-17), but a summary of the more important findings is presented below.

In earlier studies in the grant period the PPO-PS system was intensively studied by appropriate dynamical mechanical and dielectric relaxation and by calorimetric measurements. It was thus concluded that true molecular level miscibility existed in this polymer pair. It was then found possible to use isotactic PS (instead of the atactic stereoisomer) and, within certain composition ranges, induce crystallinity in the blend by appropriate thermal treatment. A combined solvent-thermal exposure unexpectedly resulted in the crystallization, in addition, of the PPO, (10). These more complex uni- or bi-crystalline blends were then studied with respect to small and large deformation mechanical properties. It was found that the melting-points of the crystalline component was systematically depressed with respect to that of the pure homopolymer. This lowering could in principle be ascribed to either a thermodynamic (melting-point depression) and/or a morphological (finite crystal size with surface effects) origin. Consequently a small- and wide-angle x-ray study was undertaken to learn more about the detailed morphology of the crystalline polymer blends, (11, 12, 13)

Additional approaches involve the use of styrene-p-chloro-styrene copolymers. Pure poly (PCS) is incompatible with PPO but an abrupt transition into the compatible regime was found to occur when the mole fraction of PS in the random copolymer became greater than 0.625. The relatively large dipole moment of PCS permitted a study of the spatial conformation of the mutually dissolved macromolecules. By measurement of the dipole orientation factor g for one of the copolymers (lying within the compatible regime) blended with PPO it was established that the characteristic radius of gyration of the constituent copolymer changed with composition in a manner similar to that found for poly (PCS) in low molecular weight solvents, thereby providing a fairly persuasive argument in favor of the molecular nature of polymer-polymer compatibility in this system, (14).

The transition properties of PS-PCS copolymer with PPO were studied in considerable detail using calorimetric and volumetric techniques, (15). The large deformation mechanical properties of these systems were also investigated; it was found that tensile strength was extremely sensitive to blend composition. It is possible that this last finding may provide an additional new criterion and test for the presence of compatibility in polymer pairs, of particular value where the T_g 's of the constituents are relatively close, (16). Transition

properties were also studied in a thermally stimulated discharge current experiment in which the polymer blends were electrically polarized above their respective T_g 's, cooled under controlled conditions, and reheated with monitoring of discharge currents ($\sim 10^{-9}$ A), (17).

F. High Pressure Studies.

Two distinct studies of properties of polymers as a function of pressure were undertaken during the grant period. In the first an apparatus was developed for the measurement of lattice parameters in polymer crystals as a function of pressure and temperature using wide-angle x-ray diffraction. The equipment consisted essentially of a rotating-anode x-ray source (silver anode), and opposed diamond anvil cell and a photographic recording system. With this equipment a complete study of the effect of pressure on high density polyethylene in the range -50°C to the melting point and at pressures from ambient to 8kb has been completed. The compressibility of the unit cell, uniquely available from diffraction measurement enabled us to compute an equation of state for the polymer crystal and compare this with ab initio calculations. Second order effects (for example the temperature dependency of the compressibility) were also obtained with reasonable precision and served as a sensitive probe for testing detailed and refined models for covalent and non-covalent interactions in the PE lattice. Although completely hydrostatic conditions cannot be guaranteed in this apparatus comparison of our data with that obtained at lower pressures using cells producing isotropic stress fields showed no errors attributable to this

source. At our highest pressures, however, a new diffraction line was observed, inconsistent with the orthorhombic lattice, indicating the presence a small fraction of a shear-induced twinning monoclinic polymer crystal over a substantial portion of P-V-T space has been reported, (18).

A second high-pressure study was concerned with dynamical mechanical studies of solid polymers. For this investigation we employed an equipment first used successfully for corresponding measurements in metals. In this apparatus the sample, in the form of a helical spring, is extended sinusoidally within a pressurized and temperature controlled vessel. The in- and out-of-phase displacements of the spring are monitored by linear differential voltage transformers and after computer processing yield $G'(\omega)$, $G''(\omega)$ or $\tan \delta$, the shear storage and loss moduli and the loss factor, respectively. Such information is useful in studying the detailed effect of chemical structure and mechanical properties of polymers. The first polymer studied was atactic polymethyl methacrylate and these measurements permitted the construction for the first time of a $\tan \delta$ -P-T surface, (19).

G. Other Studies.

A number of other studies undertaken with general AFOSR support were completed during the grant period. These included a comprehensive thermodynamic (20) and dielectric relaxation (21) study of poly(diethyl siloxane). PDES has a number of transitions in the solid state which have led to some confusion vis-à-vis a definitive identification of the glass and fusion transitions. In these studies we were able to resolve these difficulties, positively assign the questioned transitions and additionally provide evidence for an unusual intermediate liquid crystal phase. In another dielectric relaxation study the low-temperature properties of poly- ϵ -caprolactone were studied. The sub- T_g transition observed in this polymer could be correlated with mechanical measurements. The effect of the presence of traces of water--a matter of concern in polyesters--was studied. Poly- ϵ -caprolactone has been alleged to be compatible with a number of other macromolecules and this study formed part of an overall polymer-polymer miscibility investigation. Another study in this program was concerned with polypentenamer and derivatives. The addition of HCN across the double bond in this polymer yields a structure with obvious similarities to polyacrylonitrile and was thought to be compatible with, for example, PVC. (This was later found

not to be the case). The synthesis of this polymer via a hydrobromination intermediate step was studied in some detail, (23).

A series of theoretical studies, (24-26), was undertaken in the latter part of the grant period. In the first of these the thermodynamic basis for the separation of fusion entropy into configurational and constant volume terms--a procedure in wide use in both the polymer and metal areas--was critically examined and demonstrated to be incorrect. Two papers of general applicability to crystalline systems, concerned with the relation of surface to bulk properties, (25,26), were also completed. Finally mention may be made of general contributions, a book (27), a review of polymer blends, (28), and two book reviews, (29,30), that were completed in the grant period.

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20. Abstract

in a series of polymer miscibility studies in several chemically related binary systems which included poly(2,6-dimethyl phenylene oxide) (PPO)-polystyrene (PS). Thermodynamic, electrical, and mechanical properties of compatible and near-compatible systems were investigated in detail. Mechanical properties of solid polymers such as polymethyl solid polymers methacrylate under hydrostatic pressure were determined principally with respect to the transitional behavior of the amorphous phase. The effect of pressure on the equilibrium properties of the crystalline phase (high density polyethylene) was studied in a concomitant wide angle X-ray diffraction experiment. In a second dynamical mechanical study, compound flexural vibrations in thick beams of polymethyl methacrylate were measured and analyzed. It was shown that the contributions of shear and elongational deformations could be resolved thereby providing a complete isotropic elastic characterization of materials in such configurations. Finally, the method of quasi-elastic homodyne spectroscopy was used in a study of the conformational properties, including hydrodynamic and thermodynamic interactions of a solvated acrylic acid--ethyl acrylate copolymer.

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